968743

DRAFT - Quality Assurance Project Plan

ADDENDUM - 01

AECOM
SUPERVISING CONTRACTOR

FOR:
HAMILTON SUNDSTRAND CORPORATION
AREA 9/10 SOUTHEAST ROCKFORD GROUNDWATER CONTAMINATION SUPERFUND SITE
ROCKFORD, ILLINOIS

February 2021

QUALITY ASSURANCE PROJECT PLAN ADDENDUM

HAMILTON SUNDSTRAND CORPORATION
SOUTH EAST ROCKFORD AREA 9/10
WINNEBAGO COUNTY, ILLINOIS

Prepared by: AECOM

_____ _____
Mr. John Wolski
Raytheon Technologies Corporation Project Manager Date

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Mr. Peter Hollatz, P.E.
AECOM Project Manager Date

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Mr. Gregory A. Malzone
AECOM QA Manager/Project Chemist Date

_____ _____
Ms. Terese A. Van Donsel
U.S. EPA Region 5 Remedial Project Manager - CERCLA Date

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Mr. Michael McDonough
U.S. EPA Region 5 Quality Assurance Reviewer Date

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Mr. Brian Conrath
IEPA Project Coordinator Date

_____ _____
Ms. Beth Wasserman
SGS North America Project Manager Date

_____ _____
Ms. Ausha Scott
Eurofins AirToxics, Inc. QA Manager Date

1.0 PROJECT BACKGROUND

AECOM Technical Services, Inc. (AECOM) was authorized by Hamilton Sundstrand Corporation (HSC) to prepare an Addendum to the Quality Assurance Project Plan (QAPP) associated with the Remedial Action (RA) being performed at the Area 9/10 portion of the Southeast Rockford Groundwater Superfund site, Rockford, Illinois (Site). This document serves to revise/update the approved QAPP submitted in 2008 by Stantec Consulting Services, Inc. as part of the Remedial Design Work Plan for the RA (the attached figure and appendices correspond to the original QAPP) and the 2014 Addendum submitted by AECOM. The revised and updated information provided in this Addendum is required to address recent changes in project personnel and the request by United States Environmental Protection Agency (USEPA) in a letter dated January 12, 2021 to add 1,4-dioxane to the leachate monitoring program for a least one monitoring cycle.

HSC entered into a Consent Decree (CD) with the USEPA and Illinois Environmental Protection Agency (IEPA) on September 2, 1998 for the completion of a RA for source control at the HSC property within Area 9/10. HSC is in the process of performing certain actions in a manner consistent with the Record of Decision (OU3 ROD 2002) and the performance standards and requirements of the CD as more fully described in the controlling documents, including: the Statement of Work (SOW 2008), Final 100% Remedial Design (Stantec, 2007), Remedial Action Work Plan (RAWP, Stantec 2008) and USEPA-approved Remedial Action Process Flow Diagram (RAPFD).

Currently operating along the southeast boundary of the Groundwater Management Zone (GMZ) is the Phase 1 Air Sparge/Soil Vapor Extraction (AS/SVE) system. The Phase 1 AS/SVE system commenced full-scale operation on December 7, 2009. The Phase 2 AS/SVE system, currently operating within identified leachate source areas, commenced full scale operation in March 2011.

2.0 PROJECT ORGANIZATION

This section provides the project organization and associated roles including key personnel, and descriptions of duties. Figure 2 provides an organizational chart depicting the overall management approach to these activities.

2.1 USEPA

The USEPA Remedial Project Manager (RPM) is the primary point of contact for the USEPA. This individual has control over the administrative and technical aspects of the overall RA effort on behalf of the USEPA, including those regarding CERCLA matters. The USEPA RPM will coordinate activities with the IEPA Project Manager (PM) and HSC. The USEPA designated RPM is as follows:

Ms. Terese A. Van Donsel
United States Environmental Protection Agency, Region 5
77 West Jackson Blvd.
Chicago, Illinois 60604
T(312) 353-4367 F(312) 353-5541 or F(312) 886-4071

E-mail: Vandonsel.terese@epa.gov

2.2 IEPA

The IEPA will provide support to the USEPA and HSC during the performance of the RA effort. The IEPA will work closely with the USEPA as a co-signatory on the CD prescribing the RA effort. The IEPA will provide technical and administrative oversight of the RA in conjunction with the USEPA. The IEPA has identified its project manager to be as follows:

Mr. Brian Conrath
National Priorities List Unit
Federal Sites Remediation Section
Division of Remediation Management
Bureau of Land
Illinois Environmental Protection Agency
1021 North Grand Avenue East
P.O. Box 19276
Springfield, Illinois 62794-9276
T(217) 782-7592 F(815) 223-1344
E-mail: Brian.Conrath@illinois.gov

Mr. Conrath will be supported by other IEPA personnel as necessary.

2.3 HSC Project Coordinator

The HSC Project Coordinator is the designated individual to interact with USEPA and IEPA with regard to the RA efforts. The HSC Project Coordinator will be supported by additional HSC personnel as well as primary and secondary subcontracted entities. The combination of these entities under the direction of the HSC Project Coordinator will be responsible for the implementation of the activities identified in the CD. The HSC Project Coordinator for the Site is as follows:

Mr. John Wolski
Raytheon Technologies Corporation
9 Farms Springs Road
Farmington, Connecticut 06032
T(847) 221-5503
E-mail: john.wolski@rtx.com

2.4 AECOM Project Manager

The HSC Project Manager will be supported by personnel from AECOM, HSC's primary contractor, for the RA activities. AECOM has designated the following individual as the Project Manager (PM) responsible for the RA:

Mr. Peter Hollatz, PE
AECOM

1600 Perimeter Park Drive, Suite 400
Morrisville, NC 27560
T(630) 918-9648
E-mail: Peter.Hollatz@aecom.com

Mr. Hollatz will be supported by other AECOM technical, administrative, quality, and health and safety staff. In addition to AECOM personnel, various subcontractors and suppliers will be utilized in the performance of the RA effort.

2.5 Laboratory Project Managers

SGS North America Inc., Dayton, New Jersey will provide analytical laboratory services for the soil and leachate analysis. The laboratory project manager for the efforts will be:

Beth Wasserman
SGS North America Inc.
2235 Route 130
Dayton, NJ 08810
T (732) 355-4552 F(732) 329-3499
Beth.Wasserman@SGS.com

Eurofins Air Toxics, Ltd., of Folsom, California, will provide analytical laboratory services for any air analyses. The laboratory project manager for the RA efforts will be:

Ms. Ausha Scott
Eurofins Air Toxics, Ltd.
180-B Blue Ravine Rd
Folsom, CA 95630
T(916) 985-1000 F(916) 985-1020
aushascott@eurofinsus.com

2.6 AECOM Quality Assurance Manager

The Quality Assurance (QA) Manager will be responsible for ensuring that data collection and analysis is conducted in a representative manner. As appropriate, problems identified by the QA Manager will be resolved in consultation with the appropriate laboratory representative. The QA Manager will also provide third-party data validation services for this project.

Mr. Gregory A. Malzone
AECOM
Gulf Tower
707 Grant Street
5th Floor
Pittsburgh, PA 15219
T(412) 316-3524 F(412) 297-5000
E-mail: greg.malzone@aecom.com

2.7 Distribution List

The following individuals will receive copies of the approved QAPP and subsequent revisions:

Ms. Terese A. Van Donsel
United States Environmental Protection Agency, Region 5
77 West Jackson Blvd.
Chicago, Illinois 60604
T(312) 353-4367 F(312) 353-5541 or F(312) 886-4071
E-mail: Vandonsel.terese@epa.gov

Mr. John Wolski
Raytheon Technologies Corporation
9 Farms Springs Road
Farmington, Connecticut 06032
T(847) 221-5503
E-mail: john.wolski@rtx.com

Ms. Kristen Sherman
Assistant General Counsel
Raytheon Technologies Corporation
10 Farm Springs Road
Farmington, Connecticut 06032
T(860) 728-7837
E-mail: kristen.sherman@rtx.com

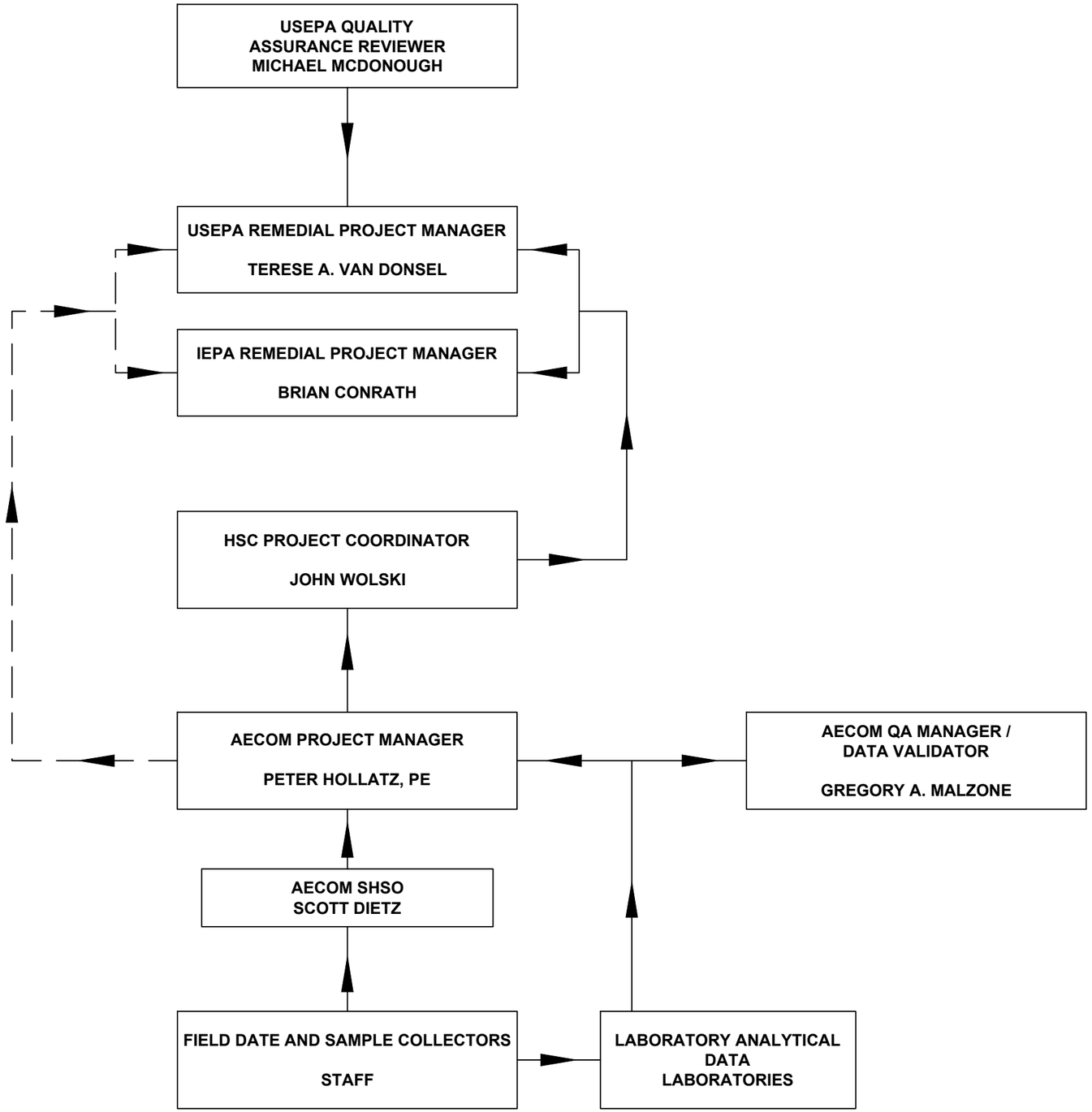
Mr. Brian Conrath
National Priorities List Unit
Federal Sites Remediation Section
Division of Remediation Management
Bureau of Land
Illinois Environmental Protection Agency
1021 North Grand Avenue East
P.O. Box 19276
Springfield, Illinois 62794-9276
T(217) 782-7592 F(815) 223-1344
E-mail: Brian.Conrath@illinois.gov

Mr. Peter Hollatz, PE
AECOM
1600 Perimeter Park Drive, Suite 400
Morrisville, NC 27560
T(630) 918-9648
E-mail: Peter.Hollatz@aecom.com

3.0 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The data quality objectives for laboratory precision, accuracy and sensitivity are listed in Appendix C of this addendum.

FIGURE 2
REVISED ORGANIZATIONAL CHART



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AECOM
27755 Diehl Road, Suite 100
Warrenville, Illinois 60555
www.aecom.com

HSC
SER AREA 9/10
Rockford, IL

Project Organization Chart

PROJ. NUMBER: 60651001

DATE: 02/08/21

DRAWING NUMBER: 1

SHEET NUMBER:

REVISION

APPENDIX C

SGS North America Inc. MDLs, RLs, and Control Limits

Compound	CAS No.	RL	MDL	Units	MS/MSD	RPD	BS	DUP
1,1,1-Trichloroethane	71-55-6	1	0.54	ug/l	74-138	12	81-128	20
1,1,2-Trichloroethane	79-00-5	1	0.53	ug/l	78-121	11	83-118	20
1,1-Dichloroethene	75-35-4	1	0.59	ug/l	63-136	14	69-126	20
1,2-Dichloroethane	107-06-2	1	0.6	ug/l	72-131	11	78-126	20
cis-1,2-Dichloroethene	156-59-2	1	0.51	ug/l	60-136	11	80-120	20
Ethylbenzene	100-41-4	1	0.6	ug/l	51-140	20	80-120	20
Tetrachloroethene	127-18-4	1	0.9	ug/l	61-139	11	70-131	20
trans-1,2-Dichloroethene	156-60-5	1	0.54	ug/l	70-126	11	76-120	20
Trichloroethene	79-01-6	1	0.53	ug/l	62-141	10	80-120	20
Vinyl chloride	75-01-4	1	0.79	ug/l	43-146	15	51-135	20

SW-846 8260D SIM

Compound	CAS No.	RL	MDL	Units	MS/MSD	RPD	BS	DUP
1,4-Dioxane	123-91-1	0.4	0.1	ug/l	36-157	42	61-125	36

RL – Reporting Limit
MDL – Method Detection Limit
MS / MSD – Matrix Spike / Matrix Spike Duplicate
RPD – Relative Percent Difference
BS – Blank Spike
DUP - Duplicate

APPENDIX D

Laboratory Standard Operating Procedures

SGS North America Inc.

LAB SUPERVISOR: C. Bryce

QA OFFICER: Marie Laschke

EFFECTIVE DATE: 1-20-2021

TITLE: METHOD 8260D, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)
REFERENCES: SW846 8260D (Revision 4, June 2018), SW846 8000D (Revision 5, March 2018)
REVISED SECTIONS: Tables 1,7 and 10 (added 1,2,3-Trimethylbenzene)

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by SGS to acquire samples for analysis of volatile organic compounds by gas chromatographic/mass spectrometric (GC/MS) following purge and trap utilizing the internal standard technique. The compounds in Table 1 may be determined by this method. An option has been included for the analysis of 1,4-Dioxane by selected ion monitoring GC/MS (GC/SIM-SIM).

1.2 This analytical method is designed for nearly all types of samples, regardless of water content, including ground water, aqueous sludges, liquors, waste solvents, oily wastes, tars, filter cakes, sediments and soils.

1.3 The applicable concentration range of this method is compound, matrix, and instrument dependent. Volatile water-soluble compounds can be included in this analytical technique. However, for some low-molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides, quantitation limits are approximately ten times higher because of poor purging efficiency. Determination of some structural isomers (i.e. xylenes) may also be hampered by coelution.

2.0 SUMMARY OF METHOD

2.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap (Method 5030/5035). Method 5030 may be used directly on ground water samples. Method 5035 is used for low-concentration and medium-concentration soils, sediments, and wastes. Medium concentration samples are preserved and stored in methanol prior to purge-and-trap analysis.

2.2 An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic (GC) column.

2.3 The volatile compounds are separated by the temperature programmed GC column and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.4 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.5 Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a calibration curve.

2.6 Additional unknown peaks with a response > 10 % of the closest internal standard may be processed through a library search with comparison to a database of approximately 75,000 spectra. An estimated concentration is quantitated by assuming a response factor of 1.

2.7 Water soluble volatile organic and other poor purging compounds maybe analyzed using this methodology, however this method is not the method of choice for these compounds and the laboratory's ability to achieve all calibration and quality control criteria for this method cannot be guaranteed. These compounds are noted as (pp) in Table 7.

2.8 The method includes an analytical option for the analysis of 1,4-Dioxane by GC/MS-SIM. The selected ions that are characteristic of the analytes of interest are analyzed using lower concentrations of calibration standards under the same MS conditions. SIM analysis is performed upon client request and is documented in the report.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve and may vary depending on matrix interferences, sample volume or weight and percent moisture. Detected concentrations below this concentration cannot be reported without qualification. See Table 10.

3.1.1 Compounds detected at concentrations between the reporting limit and MDL are quantitated and qualified as "J", estimated value. Program or project specifications may dictate that "J" qualified compounds are not to be reported.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B, revision 2. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

3.2.3 Calculated MDLs may not be feasible in the analysis of samples, particularly in regard to compounds in table 11 and common laboratory solvents (methylene chloride and acetone). In these cases, the MDLs may be raised from the calculated value to a maximum of half the LOQ to avoid false positives being reported.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. See individual types of Blanks: Method Blank, Instrument Blank, Storage Blank, Cleanup Blank and Sulfur Blank.

4-BROMOFLUOROBENZENE (BFB) - the compound chosen to establish mass spectral instrument performance for volatile (VOA) analyses.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

EXTRACTED ION CURRENT PROFILE (EICP) - a plot of ion abundance versus time (or scan number) for ion(s) of specified mass (Es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, sample (for volatiles), and sample extract (for semivolatiles) at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is distinguishable from method blank results.

PERCENT DIFFERENCE (%D) - As used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

PRIMARY QUANTITATION ION - a contract specified ion used to quantitate a target analyte.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph: a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

INSTRUMENT BLANK – a system evaluation sample containing lab reagent grade water with internal standards and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the SGS Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the

chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device must be avoided.

6.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

6.4 Contamination by carry-over can occur whenever high level and low-level samples are sequentially analyzed.

6.4.1 Whenever an unusually concentrated sample is encountered, it must be followed by an analysis of an instrument blank to check for cross contamination. Refer to Table 11 for compounds that may cause carryover for this method.

6.4.2 It may be necessary to wash the purging device with methanol, rinse it with organic-free water, and then dry the purging device in an oven at 105^0 C. Follow the instrument manual for instructions on cleaning. Document the occurrence in the maintenance log and notify the manager/supervisor.

6.4.2.1 Clean and bake purging tube.

6.4.2.2 Clean or replace purge needle.

6.4.2.3 Clean and bake sample filter or sparge filter.

6.4.2.4 Clean and bake sample loop.

6.4.2.5 Replace trap if necessary.

6.4.2.6 Replace water management module if necessary.

6.4.2.7 Rinse transfer line with methanol. Caution: disconnect the trap before rinsing.

6.4.3 In extreme situations, the entire purge-and trap device may require dismantling and cleaning. Follow the instrument's manual for instructions on disassembly. Document the occurrence in the maintenance log and notify the manager/supervisor. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples.

6.4.4 If the contamination has been transferred to gas chromatograph, any of the following approaches may be used to cleanup the instrument.

6.4.4.1 Baking out the column between analyses.

6.4.4.2 Change the injector liner to reduce the potential for cross-contamination.

6.4.4.3 Remove a portion of the analytical column in the case of extreme contamination.

6.4.5 The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are stripped from the chromatographic column.

6.5 Special precautions must be taken during the analysis to avoid contamination from methylene chloride and other common laboratory solvents.

6.5.1 The sample storage and analytical area must be isolated from all atmospheric sources of methylene chloride or other common solvents.

6.5.2 Laboratory clothing worn by the analyst must be clean and used in designated areas only. Clothing previously exposed to solvent vapors in the organics sample preparation laboratory can contribute to sample contamination.

6.6 Samples with suspected or known permanganate levels must be preserved with ascorbic acid at collection. The purpose of the ascorbic acid is to remove the permanganate which is an oxidizer. There is potential that the analytes of concern will undergo an oxidative transformation which would no longer be representative of the concentrations as the site.

7.0 SAMPLE HANDLING AND PRESERVATION AND HOLDING TIME

7.1 HANDLING and PRESERVATION

7.1.1 Water samples

7.1.1.1 Container - 40 ml glass screw-cap VOA vial with Teflon-faced silicone septum. The 40-ml glass VOA vials are pre-cleaned and certified.

7.1.1.2 Acrolein & Acrylonitrile

7.1.1.2.1 If acrolein and acrylonitrile are to be analyzed, collect 3, 40 mL VO vials of sample unpreserved. Samples for acrolein and acrylonitrile analysis receiving no pH adjustment must be analyzed within 7 days of

sampling. All samples must be footnoted stating samples were unpreserved and analyzed within 7 days.

7.1.1.3 Collect all samples in triplicate. Test all samples for residual chlorine using test paper for free and total chlorine. If samples contain residual chlorine, three milligrams of sodium thiosulfate must be added for each 40 ml of water sample.

7.1.1.4 Fill sample bottles to overflowing, but do not flush out the dechlorinating agent. Sample must be taken with care so as to prevent any air or bubbles entering vials creating headspace.

7.1.1.5 Adjust the pH of all samples to ≤ 2 at the time of collection, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 ml of sample. Seal the sample bottles, Teflon face down, and mix for one minute. Or VOA vials containing the preservative (HCL) may be used.

Note: Do not mix the sodium thiosulfate with the HCl in the sample bottle prior to sampling.

7.1.1.6 The samples must be protected from light and refrigerated at 0 - ≤ 6 °C from the time of receipt until analysis.

7.1.1.7 An alternate preservative that may be used when suspected or known levels of permanganate exist in a sample is 25 mg of ascorbic acid per 40 ml vial.

7.1.1.7.1 Ascorbic acid is added to remove the permanganate which is an oxidizer.

7.1.1.7.2 Fill the sample bottles to overflowing, but do not flush out the ascorbic acid.

7.1.1.7.3 The samples must be protected from light and refrigerated at 0 - ≤ 6 °C from the time of receipt until analysis.

7.1.2 Soil Samples

7.1.2.1 Refer to the SOP for SW846 Method 5035 for preservation requirement of non-aqueous solids.

7.2 HOLDING TIME

7.2.1 Water Samples.

7.2.1.1 All samples are to be analyzed within 14 days of sampling (HCl preserved for aqueous sample) unless otherwise specified by the contract. The sample preservation deficiency is noted in the analytical run logbook when the analyst checks the pH at the bench. If the pH is not <2, the analyst notifies the supervisor, who then notifies Client Service Dept. A comment is added to the result page and Non-Conformance Summary.

7.2.1.2 Acrolein & Acrylonitrile

7.2.1.2.1 Samples for acrolein and acrylonitrile analysis receiving no pH adjustment must be analyzed within 7 days of sampling.

7.2.2 Soil Samples

7.2.2.1 Refer to the SOP for SW846 Method 5035 for holding time requirement of non-aqueous solids.

7.2.2.2 All samples are analyzed within 14 days of sampling unless otherwise specified.

8.0 APPARATUS AND MATERIALS

8.1 SYRINGE

8.1.1 10, 25, 50, 100, 250, 500, 1000 and 5000 µl graduated syringes, held manually (Hamilton/equiv.).

8.1.2 5 ml and 50 ml glass gas tight syringes with Luerlok end, if appropriate for the purging device.

8.2 BALANCE

8.2.1 Analytical balance capable of weighing 0.0001 gram.

8.2.2 Top loading balance capable of weighing 0.1 gram.

8.3 PURGE AND TRAP DEVICES

8.3.1 The autosampler models are used for purging, trapping and desorbing the sample into GC column.

- O.I. Model 4560 sample concentrator with 4551 vial multi-sampler
- O.I. Model 4560 sample concentrator with 4552 Water/Soil multi-sampler
- EST Analytical Encon Evolution concentrator with EST Centurion multi-sampler

8.3.2 The sample purge vial must be designed to accept 5 ml of sample with a water column at least 3 cm deep.

8.3.3 The auto-sampler is equipped with a heater capable of maintaining the purge chamber at 40 °C to improve purging efficiency. The heater is to be used for low level soil/sediment analysis, but not for water or medium level soil/sediment analysis.

8.3.4 The OI #10 trap is 42 cm with an inside diameter of 0.105 inches. The trap must be packed to contain the following absorbents (3-ring) and must be conditioned at 210 °C for 30 minutes by backflushing with a Helium or Nitrogen gas flow at least 20 ml/min before initial use.

- Tenax (2,6-Diphenylene oxide polymer).

- Silica gel.
- Carbon Molecule Sieve (CMS).

8.3.5 The EST K trap for EST instruments. (Condition as per manufacturer's directions).

8.3.6 The desorber must be capable of rapidly heating the trap to 190^0 C for desorption. Do not exceed 210^0 C during bake-out mode. Alternatively, follow manufacturer's instructions.

8.4 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

8.4.1 Gas Chromatograph.

8.4.1.1 An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

8.4.1.2 The injection port must be suitable for split or splitless with appropriate interface.

8.4.1.3 The narrow bore capillary column is directly coupled to the source for HP-6890/7890 or Agilent 6890/7890 model.

8.4.1.4 The wide bore capillary column is interfaced through a jet separator to the source for HP-5890 model.

8.4.2 Column.

- 75 m x 0.53mm ID x 3 μm film thickness capillary column coated with DB-624 (J&W Scientific), or equivalent. Condition as per manufactures directions.
- 105 m x 0.53mm ID x 3 μm film thickness capillary column coated with HP-VOA, or equivalent. Condition as per manufactures directions.
- 60 m x 0.25mm ID x 1.4 μm film thickness capillary column coated with DB-624 (J&W Scientific), or equivalent. Condition as per manufactures directions.
- 60 m x 0.45mm ID x 1.7 μm film thickness capillary column coated with DB-VRX (J&W Scientific), or equivalent. Condition as per manufactures directions.
- 30 m x 0.25mm ID x 1.4 μm film thickness capillary column coated with RTX-624, or equivalent. Condition as per manufactures directions.
- 20 m x 0.25mm ID x 1.4 μm film thickness capillary column coated with RTX-624, or equivalent. Condition as per manufactures directions.

8.4.3 Mass Spectrometer.

8.4.3.1 HP5973, HP5970 Agilent 5973, or Agilent 5975 is capable of scanning from 35 to 270 amu every 2 seconds or less, utilizing 70-volt (nominal) electron energy in the electron impact ionization mode.

8.4.3.2 The mass spectrometer must be capable of producing a mass spectrum which meets all the criteria in Table 3 when injecting or purging 50 ng of the GC/MS tuning standard - Bromofluorobenzene (BFB).

8.4.3.3 SIM Mode – Capable of selective ion grouping at specified retention times for applications requiring quantitation limits below the normal range of electron impact mass spectrometry or for increased compound sensitivity (Table 2a).

8.5 DATA SYSTEM

8.5.1 Data Acquisition and Instrument Control (HP Chemstation) **-** A computer system is interfaced to the mass spectrometer, which allows the continuous acquisition and storage on a machine-readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

8.5.2 Data Processing (HP Enviroquant) - The software accommodates searching of GC/MS data file for target analytes which display specific fragmentation patterns. The software also allows integrating the abundance of an EICP between specified time or scan number limits. The data system includes the recent version of the EPA/NBS or NIST98 mass spectral library for qualitative searches of non-target compounds present in the chromatogram. The data system flags all data files that have been edited manually by laboratory personnel.

8.5.3 Off-line Magnetic Tape Storage Device (Lagato Networker) - The magnetic tape storage device copies data for long-term, off-line storage.

9.0 REAGENTS AND STANDARDS

9.1 Solvent

9.1.1 Methanol: purge-and-trap grade quality or equivalent. Store separately, away from the other solvents.

9.2 Reagent Water

9.2.1 Reagent water is defined as water in which an interferant is not observed at the method detection limit of the parameters of interest.

9.2.2 Reagent water is generated by either passing tap water through a bed of approximately one pound of activated carbon or by using the water purification system at SGS that is a series of deionizers and carbon cartridges.

9.3 Stock Standard Solutions

9.3.1 Commercially prepared standards used.

9.3.1.1 EPA Method 524.2 Volatiles (78 components): Absolute (or equivalent) at 200 μg/ml or 2,000 μg/ml concentration.

9.3.1.2 Custom Volatiles Mix A: Restek (or equivalent) at 2,000 μg/ml concentration.

9.3.1.3 Custom Volatiles Mix B: Restek (or equivalent) at 2,000 - 100,000 μg/ml concentration.

9.3.1.4 VOC Gas Mixture: Restek (or equivalent) contains 200 μg/ml or 2,000 μg/ml of the following compound**s** in methanol.

- Bromomethane
- Chloroethane
- Chloromethane
- Dichlorodifluoromethane
- Trichlorofluoromethane
- Vinyl Chloride

9.3.1.5 Multiple neat compounds and individual compounds at varying concentrations in methanol.

9.3.1.6 Surrogate standard mixture: Absolute (or equivalent) at a concentration of 10,000 μg/ml each surrogate compound.

- 1,2-Dichloroethane-d_4
- Dibromofluoromethane
- Toluene-d_8
- 4-Bromofluorobenzene

9.3.1.7 Internal standard mixture: Sigma-Aldrich (or equivalent) neat compounds diluted to 20,000 μg/ml except Tert Butyl Alcohol-d_9, which is diluted to a concentration of 50,000 μg/ml. The following five internal standards are used that exhibit similar analytical behavior to the compounds of interest.

- 1,4-Dichlorobenzene-d_4
- 1,4-Difluorobenzene
- Chlorobenzene-d_5
- Pentafluorobenzene
- Tert Butyl Alcohol-d_9

9.3.1.8 1,4-Dioxane Solution for SIM: Absolute (or equivalent) at 100 μg/ml in methanol.

9.3.1.9 Ketones mixture: Absolute (or equivalent) at 20,000 μg/ml for Acetone, 2-Butanone, 4-methyl-2-pentanone (MIBK), and 2-hexanone prepared at concentrations 300 ug/ml for soil matrix and 300 ug/ml for aqueous matrix.

9.3.2 Unopened stock standard (ampoules) must be stored according to manufacturer's documented holding time and storage temperature recommendations (usually placed on the ampoule).

9.3.3 After opened, stock standards, internal standards, and surrogate solutions must be replaced after 6 months (one month for purgeable gases standard) or sooner if

manufacture expiration date come first or comparison with quality control check samples indicates degradation.

9.3.4 Store all stock standards in vials with minimal headspace and Teflon lid liners after open, protect from light, and refrigerate to –10°C or colder or as recommended by the standard manufacturer.

9.3.5 Return the standards to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

9.4 Internal Standard and Surrogate Solution

9.4.1 Five internal standard and surrogate spiking solutions are prepared in methanol per Table 8.A.

9.4.1.1 25 μg /ml internal standard and surrogate mixture.

9.4.1.2 250 μg /ml internal standard and surrogate mixture.

9.4.1.3 100 μg/ml surrogate mixture.

9.4.1.4 25 μg /ml internal standard mixture.

9.4.1.5 250 μg /ml internal standard mixture.

9.4.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.4.3 Each 5 ml sample, QC sample, and blank undergoing analysis must be spiked with any one of the above spiking solutions (depending upon the type of standards addition modules used), resulting in a concentration of 50 μg/l of each compound.

9.4.4 Prepare fresh internal standard and surrogate spiking solutions every six months, or sooner, if manufacturer's expiration dates come first or if the solution has degraded or evaporated.

9.5 Secondary Dilution Standards

9.5.1 Using stock standard solutions prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together.

9.5.1.1 100 μg/ml V8260 (ABK) mixture: prepared from 2,000 μg/ml stock solution and mixtures from neat compounds prepared in-house. (see Table 8-C)

9.5.1.2 100 μg/ml V8260 Acrolein: prepared from 90-95% neat compound. (see Table 8-C)

9.5.1.3 100 μg/ml Gas mixture: prepared from 2,000 μg/ml stock solution. (see Table 8-C)

9.5.2 Replace after one month for non-gas mixtures (one week for gas mixtures) or sooner if manufacture expiration date come first or comparison with quality control check samples indicates degradation.

9.5.3 Store all secondary dilution standards in vials with no headspace and Teflon lid liners, protect from light, and refrigerate to – 10°C or colder or according to manufacturer's storage temperature recommendations.

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9.5.4 Return the standards to the freezer as soon as preparation is finished to prevent the evaporation of volatile compounds.

9.6 Aqueous Calibration Standard Solutions

9.6.1 Initial Calibration Standards

9.6.1.1 Prepare a minimum of five aqueous calibration standard solutions containing the surrogate compounds as Table 8-D.1 or 8-D.2.

9.6.1.2 To prepare a calibration standard, add a measured volume of secondary dilution standard solutions and the surrogate spiking solution to an aliquot of reagent water in the flask. Use a micro-syringe and rapidly inject the methanol standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Bring to volume. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask.

9.6.1.2.1 1,4-Dioxane for SIM analysis is prepared from primary stock standard (100ppm).

9.6.2 Continuing Calibration Standard

9.6.2.1 A continuing calibration standard at a concentration of 50 μg/l is prepared as the scheme outlined in Table 8-E.

9.6.3 Aqueous standards are not stable and may be stored up to 24 hours if held in Teflon sealed screw-cap vials with zero headspace at 4^0C ($\pm$ 2^0C). Protect the standards from light. If not so stored, they must be discarded after use, unless they are set up to be purged by an autosampler.

9.6.4 When using an autosampler, standards may be retained up to 12 hours if they are in purge tubes connected via the autosampler to the purge and trap device.

9.7 Second Source Calibration Check Standard (ICV)

9.7.1 Prepare the second source calibration check standards from separate manufacturer source or from a manufacturer's batch prepared independently from the batch used for calibration curve following the procedures in Section 9.6. At a minimum, an ICV must be analyzed with every initial calibration.

9.7.2 For 1,4-Dioxane via SIM: Prepare the second source calibration check standard using 20 µl of a 100ppm (Absolute or equivalent) to 100 mL of reagent water which yields a 20 ppb standard.

9.8 4-Bromofluorobenzene (BFB) Standard

9.8.1 Two BFB solutions are prepared in methanol per Table 8-B.

9.8.1.1 25 µg /ml solution for direct injection.

9.8.1.2 250 µg /ml solution for purging.

9.8.2 The solution must be replaced after 6 months or sooner if mass spectrum indicates degradation or if manufacture expiration date comes first.

9.9 Ascorbic Acid

10.0 CALIBRATION

10.1 Daily Maintenance. Routine Daily maintenance must be performed before any tuning, calibration or sample analysis activities are initiated. These include checks of the following items:

Purge and Trap Device:

Clean & bake purge tube
Bake trap and transfer lines
Check or refill internal/surrogate spike solution on SIM/SAM vials
Clean/replace syringe (if necessary)
Change and refill rinse bottle
Empty and rinse waste bottle

GC Oven: (if necessary)

Change septum
Change liner
Clip column, indicated by carbon build-up

10.2 Initial Calibration

10.2.1 The calibration range covered for routine analysis under RCRA, and SIM, employs standards of 0.2, 0.5, 1(specified compounds only), (2)*, 5, 10, 20, 50, 100, 200,(300 or 400)* µg/l. (*instrument dependent). Optionally 4 and 8 ug/l standards may replace the 5 and 10 ug/l standards. A minimum of five standards must be run sequentially. The low calibration standard defines the reporting limit. Lower concentration standards (0.2, 0.5, 1.0 or 2.0 µg/l) may be needed to meet the reporting limit requirements of state specific regulatory programs. Refer to Table 8-D-1 and 8-D-2 for calibration standard preparation.

10.2.2 The surrogates are introduced to the calibration standards automatically by the autosampler. For this calibration option the surrogate linear response is less

important, since multiple concentrations of surrogates are not being measured. Instead, the surrogate concentration remains constant throughout and the recovery of this known concentration can easily be attained without demonstrating if the response is linear.

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10.2.2.1 Optional: The surrogates can be added manually. In order to compensate for the difference between the automatic and manual surrogate additions a correction factor must be applied to the amount of surrogate added in Table 8-D. To determine the correction factor divide the surrogate concentration from an automatic injection by the surrogate concentration from a manual injection for each of the surrogates. Average the result for each of the surrogates to determine the correction factor. Finally multiply the correction factor by the appropriate amount of surrogate from Table 8-D and add this amount to the standard.

10.2.3 For water and medium-level soil calibration: Transfer and fill up (no air space) each standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

10.2.4 For low-level soil calibration: Transfer 5 ml of each standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

10.2.4.1 When calibrating for Method 5035 low-level samples, if the sodium bisulfate option was used, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of each standard into vial otherwise do not add sodium bisulfate. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds. Cap the vial with Teflon septum and place it into O.I sample tray.

10.2.5 The linear range covered by this calibration is the highest concentration standard.

10.2.6 Program the autosampler to add internal standard mixture (and optionally surrogate) to each standard. This results in a concentration of 50 μg/l for each internal standard (and surrogate).

10.2.6.1 For O.I. SIM spiker: Automatically adds 5 μl of 50 μg/ml internal standard solution **(**Section 9.4.1.4) or Internal Standard/Surrogate solution (Section 9.4.1.1) to each standard.

10.2.6.2 For O.I. SAM spiker: Automatically adds 1 μl of 250 μg/ml internal standard solution (Section 9.4.1.5) or Internal Standard/Surrogate solution Section 9.4.1.2) to each standard.

10.2.7 Analyze the standard solutions using the conditions established in Section 11.0. Whenever the highest concentration standard is analyzed, it is usually followed by the analyses of two reagent water blanks. Further analysis may not proceed until the blank analysis is demonstrated to be free of interferences.

10.2.8 Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 7.

10.2.9 The Response Factor (RF) is defined in Section 13.1. Calculate the mean RF for each target analyte using minimum of five RF values calculated from the initial calibration curve.

10.2.10 For the initial calibration to be valid, the following criteria must be met.

10.2.10.1 The percent relative standard deviation (% RSD) (see Section 13.2) of all target analytes must be less than or equal to 20%.

10.2.10.2 If the average response factor criteria cannot be achieved, and if the problem is associated with one or more of the standards, reanalyze the standards and recalculate the RSD. The instrument logbook must have clear documentation as to what the suspected problem was.

10.2.10.3 Alternately, if the average response factor criteria cannot be achieved, the calibration range can be narrowed by dropping the low or high point of the curve. Multiple levels may be removed, but removal of interior levels is not permitted

10.2.10.3.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end.

10.2.10.3.2 The laboratory may remove an entire single standard calibration level from the interior of the calibration curve when the instrument response demonstrates that the standard was not properly introduced to the instrument, or an incorrect standard was analyzed. If a calibration standard was removed from the interior of the calibration, this particular standard calibration level must be removed for all analytes. Removal of calibration points from the interior of the curve is not to be used to compensate for lack of maintenance or repair to the instrument.

10.2.10.3.2.1 The laboratory must adjust the LOQ/reporting limit and quantitation range of the calibration based on the concentration of the remaining high and low calibration standards.

10.2.10.3.2.2 The laboratory must ensure that the remaining initial calibration standards are sufficient to meet the minimum requirements for number of initial calibration points as mandated by the method, or regulatory requirements.

10.2.10.3.2.3 The laboratory may replace a calibration standard provided that:

a) the laboratory analyzes the replacement standard within twenty-four (24) hours of the original calibration standard analysis for that particular calibration level;

b) the laboratory replaces all analytes of the replacement calibration standard if a standard within the interior of the calibration is replaced;

c) the laboratory limits the replacement of calibration standards to one calibration standard concentration.

10.2.10.3.2.4 The laboratory must document a technically valid reason for either removal or replacement of any interior calibration point.

10.2.10.4 If the average response factor criteria still cannot be achieved, employ an alternative calibration linearity model. Specifically, linear regression using a least squares approach may be employed.

10.2.10.4.1 If linear regression is employed select the linear regression calibration option of the mass spectrometer data system. Forcing the calibration model through the origin (for analytes that are consistently detected in the blanks) allows for a better estimate of the background level of blank contaminants. An accurate estimate of background contamination is necessary to set method reporting limits for analytes when blank levels are problematic.

10.2.10.4.2 The correlation coefficient (r value) must be ≥0.99 for each compound to be acceptable. The calculation of relative error (%RE) must be performed for two calibration levels (near the mid-point of the initial calibration and the standard at the lowest level):

$$\%\ Relative\ Error = \frac{x'_i - x_i}{x_i} \times 100$$

x_i = True value for the calibration standard
x'_i = Measured concentration of the calibration standard

10.2.10.4.2.1 When calculating the calibration curves using the linear regression model, two quantitation checks must be performed by re-fitting the response from the standard at or near the mid-point of the initial calibration and the standard at the lowest level back into the curve.

10.2.10.4.2.2 The recalculated concentration of these two quantitation checks must be within ± 30% of the standard's true concentration for mid-point and ±50% for lowest level.

10.2.10.5 The initial calibration criteria for this method apply to all additional compounds of concern specified by the client.

10.2.10.6 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient for the linear calibration option, then the chromatographic system is considered too reactive for the analysis to begin. Perform corrective action and recalibrate if the calibration criteria cannot be achieved.

10.2.10.7 A quadratic calibration model is allowed if the linear regression fails.

10.2.10.7.1 This may only be used for historically poor performing compounds (e.g. ketones).

10.2.10.7.2 A minimum of six calibration points is required. Do not employ 0,0 as a calibration point.

10.2.10.7.3 Quadratic calibration models cannot be used to extend the calibration range.

10.2.10.7.4 The calculation of relative error (%RE) must be performed for two calibration levels- the standard at or near the mid-point of the initial calibration and the standard at the lowest level. The relative error at the lowest level must be within ± 50% of the standard's true concentration, and at the mid-point it must be ±30% of the true concentration.

10.2.10.8 It is recommended that the minimum response factor for the most common target analytes in table 12 must be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Poor purging compounds such as ketones may not meet the recommendations.

10.3 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

10.3.1 The calibration is verified with a calibration check standard at 50 μg/l from an external source (Section 9.7). It must be analyzed immediately following the initial calibration.

10.3.2 The percent difference (% D) (Section 13.3) for this standard must meet the criteria of 30% for all the target compounds.

10.3.2.1 If % D is greater than 30%, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.3.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other and repeat the initial calibration.

10.4 Continuing Calibration Verification Standard (CCV)

10.4.1 A continuing calibration verification standard at a concentration near mid-level of the initial calibration range (50 μg/l) must be acquired every 12 hrs or at the beginning of each analytical batch. If samples are analyzed within twelve hours of initial calibration, the CCV may be omitted, and injection of the last ICal standard may be used as the starting time reference for evaluation.

10.4.1.1 For water and medium level soil analysis: Transfer and fill up (no air space) the calibration verification standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray. Analyze as per Section 11.7.

10.4.1.1.1 Vary the concentration of the continuing calibration verification standard on alternate verifications (i.e. every other calibration verification) using an

alternative concentration standard. The standard selected must be lower than the midpoint calibration standard.

10.4.1.2 For low-level soil analysis: Transfer 5 ml of the calibration verification standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray. Analyze as per Section 11.7.

10.4.1.2.1 When calibrating for Method 5035 low-level samples, if the sodium bisulfate option was used add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the calibration verification standard into vial, otherwise do not use sodium bisulfate. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds. Analyze as per Section 11.7.

10.4.1.3 A continuing calibration standard is analyzed whenever the analyst suspects that the analytical system is out of calibration. If the calibration cannot be verified, corrective action is performed to bring the system into control. Analysis may not continue until the system is under control.

10.4.2 For the continuing calibration to be valid, all of the following specified criteria must be met.

10.4.2.1 Each of the most common target analytes in the calibration verification standard must meet the minimum response factors as noted in Table 12.
This criterion is particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration.

10.4.2.2 All target compounds of interest must be evaluated using a 20%variability criterion. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid.

10.4.2.3 Due to the large numbers of compounds that may be analyzed by this method, some compounds will fail to meet the criteria. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples.

10.4.2.4 In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

10.4.2.4.1 Compounds with response factors that exceed the 20% D in the CCV compared to the initial calibration with high bias may only be reported as an estimated value.

10.4.2.4.2 Compounds that do not meet the 20% D in the CCV compared to the initial calibration due to low response factors can only be reported if the low sensitivity of the instrument is still achieved. This sensitivity must be verified by running a low-level standard check at the RL. If a positive result for the compound is found, then adequate sensitivity has been demonstrated and the run can proceed. Non-detect results for samples may be reported, positive results, if reported, must be done as an estimated value.

10.4.3 If the first continuing calibration verification (CCV) does not meet criteria, a second standard can be analyzed immediately or after the corrective action was performed. If the second CCV fails to meet criteria, then corrective actions must be performed. Such as: auto-tuning, routine system cleaning and routine system maintenance. Notify the team leader/manager.

10.4.3.1 If the second CCV trial fails, the lab must demonstrate acceptable performance after corrective action with two consecutive passing calibration verifications (CCVs) OR a new initial calibration. The Instrument Logbook and Maintenance Logbook must have clearly documented notations as to what the problem was and what corrective action was implemented.

10.4.3.1.1 If the lab has not verified calibration, samples cannot be analyzed.

10.4.3.1.2 However, in the case where samples are analyzed on the system where the CCV does not meet the criteria the data must be flagged.

10.4.3.1.2.1 The data may be usable if the response for the verification exceed high (high bias) and the associated samples are non-detects.

10.4.3.1.2.2 If the criteria for the CCV is low (low bias), those sample results may be reported only if they exceed a maximum regulatory limit/decision level.

10.4.3.2 If the calibration verification is being performed using an auto sampler for night batch, two (2) vials of standard solution are placed in the device for analysis. The second standard must meet continuing calibration criteria and is used for calibration verification. The second check may be discarded only if there is a purge failure or incorrect spike concentration provided the first calibration standard meets the requirement. In this case, the first calibration standard is used as calibration verification following team leader/manager approval. Document this occurrence on instrument log.

10.4.3.2.1 Both CCVs must be evaluated. If vial 1 fails and vial 2 passes this meets the criteria of 10.4.3 of consecutive and immediate passing CCV.

10.4.3.2.2 If CCV number 2 fails, the analysis cannot continue unless it was determined that there was an isolated mechanical failure.

10.4.4 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or the retention time changes by more than 30 seconds from the midpoint standard of the last initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

10.4.4.1 Reanalyze the continuing calibration standard. New initial calibration is required if reanalyzed standard continues to fail the internal standard requirements.

10.4.4.2 All samples analyzed while the system was out of control must be reanalyzed following corrective action.

10.5 Corrective Action Maintenance for Failed Tuning and Calibration Procedures

10.5.1 Inability to achieve criteria for instrument tuning or calibration may indicate the need for instrument maintenance. Maintenance may include routine system cleaning and replacement of worn expendables or the need for outside service if the scope of the repair exceeds the capability of the staff.

10.5.2 If maintenance is performed on an instrument, return to control must be demonstrated before analysis can continue. Return to control is demonstrated as follows:

10.5.2.1 Successful instrument tune using PFTBA.

10.5.2.2 Successful tune verification by the analysis of 4-bromofluorobenzene.

10.5.2.3 Successful initial calibration or continuing calibration.

11.0 PROCEDURE

11.1 Instrument conditions.

11.1.1 Recommended instrument conditions are listed in Table 2 and 2a (SIM only). Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification must be approved by team leader/manger.

11.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, use the same GC conditions for the analysis of all standards, blanks, samples, and QC samples.

11.2 Purge and Trap Device conditions.

11.2.1 See Table 2.

11.2.2 Daily Maintenance. Routine Daily maintenance must be performed before any tuning, calibration or sample analysis activities are initiated. These include checks of the following items:

<u>Purge and Trap Device:</u>

- Clean & bake purge tube.
- Bake trap and transfer lines.
- Check or refill internal/surrogate spike solution on SIM/SAM vials.
- Clean/replace syringe (if necessary).
- Change and refill rinse bottle.
- Empty and rinse waste bottle.

11.3 Step 1: Daily GC/MS performance check.

- Inject 50ng of BFB solution directly on column or
- Purge 50ng/mL of BFB solution onto the GC column.

11.3.1 The GC/MS system must be checked to verify acceptable performance criteria are achieved (see Table 3).

11.3.2 This performance test must be passed before any samples, blanks or standards are analyzed. Evaluate the tune spectrum by selecting the mass spectrum at the peak apex or by using an average spectrum (e.g., three highest abundance spectra, or across entire BFB peak).

11.3.3.1 Select the scans at the peak apex and one to each side of the apex.

11.3.3.2 Calculate an average of the mass abundances from the three scans.

11.3.3.3 Background subtraction is allowed. Select a single mass spectrum or an average mass spectrum across a short time range acquired within 20 seconds of the elution of BFB. The background subtraction must be used only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

11.3.3 If all the criteria are not achieved, the analyst must retune the mass spectrometer with team leader/manager and repeat the test until all criteria are met.

11.3.4.1 Alternatively, an additional scan on each side of the peak apex may be selected and included in the averaging of the mass This will provide a spectrum of five averaged scans centered on the peak apex. NOTE: The selection of additional mass scans for tuning may only be performed with supervisory approval on a case by case basis.

11.3.4.2 Note: All subsequent standards, samples, MS/MSDs, BS, and blanks associated with a BFB analysis must use identical mass spectrometer conditions.

11.3.4.3 The injection time of the acceptable tune analysis is considered the start of the 12-hour clock.

11.3.5 The BFB must meet the criteria before sample analysis begins. The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

11.4 Step 2: Daily calibration check

11.4.1 Initial calibration

11.4.1.1 Refer to Section 10.2.

11.4.1.2 An initial calibration must be established (or reestablished) on each instrument:

- Prior to any sample analyses;
- Whenever a new column is installed;
- Whenever instrument adjustments that affect sensitivity are made; and
- Whenever a continuing calibration standard fails to meet the specified acceptance criteria, on the second trial.

11.4.2 Initial Calibration Verification - Second Source Calibration Check Standard

11.4.2.1 This standard is only analyzed when initial calibration provided. Refer to Section 10.3.

11.4.3 Continuing Calibration verification standard

11.4.3.1 Refer to Section 10.4.

11.4.4 The method blank (step 3) cannot be analyzed until the continuing calibration verification meets the criteria.

11.5 Step 3: Method blank

11.5.1 The acceptable method blank must be analyzed for every 12-hour time period or sooner.

11.5.1.1 Water and medium-level soil samples - Place a 40 ml vial, filled with DI water onto the autosampler.

11.5.1.2 Low-level soil samples without sodium bisulfate - Transfer 5 ml of DI water to a 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.5.1.2.1 Low-level soil samples with sodium bisulfate (Method 5035) - Add 1g of sodium bisulfate into a 40 ml vial before adding 5 ml of DI water. Cap the vial with a Teflon septum, then place the vial onto the autosampler.

11.5.2 Program the autosampler to add internal standard and surrogate solution to the method blank for a concentration of 50 µg/l for each internal standard and surrogate.

11.5.2.1 For O.I. SIM spiker: Automatically adds 10 µl of 25 µg/ml internal standard and surrogate solution (Section 9.4.1.1) to the method blank.

11.5.2.2 For O.I. SAM spiker: Automatically adds 1 µl of 250 µg/ml internal standard and surrogate solution (Section 9.4.1.2) to the method blank.

11.5.3 No compound can be present above the laboratory's MDL. Common laboratory solvents (i.e. methylene chloride, acetone, hexane) may be present up until the RL. Blanks may contain analyte concentrations greater than acceptance limits if the associated samples in the batch are unaffected (i.e., targets are not present in samples or sample concentrations are ≥10x the blank).

11.5.4 Surrogates must meet recovery criteria specified in house limits.

11.5.5 If the method blank does not meet surrogate criteria or contains target analytes above the MDL, then

11.5.5.1 All samples analyzed following an out of control method blank must be reanalyzed if conditions in 11.5.3 are not met.

11.5.5.2 Check for the potential of contamination interference from the following areas. Make sure all items are free contamination.

- the analytical system,
- dust and vapor in the air,
- glassware and
- Reagents.

11.5.5.3 Re-analyze the method blank following the system evaluation. In this situation, the instrument logbook must have clearly documented notations as to what the problem was and what corrective action was implemented to enable the second blank to pass.

11.5.5.4 If re-analyzed method blank remains out of control, notify team leader or manager.

11.5.6 If two consecutive method blanks are analyzed during unattended operations, the second analysis must meet criteria for the subsequent sample analysis to be valid. Always report the second method blank. The second analysis can only be discarded because of a purge failure provided that the first blank meets the requirement. In this case, the first blank is reported following team leader/manager approval. Document this occurrence on the instrument log.

11.5.7 Re-analysis is not necessary if the analyte concentration falls well below the action or regulatory limit or if the analyte is deemed not important for the project.

11.6 Step 4: Blank spike (BS)

11.6.1 An acceptable blank spike must be analyzed with every analytical batch. The maximum number of samples per analytical batch is twenty.

11.6.2 Spike 50 ml of reagent water with appropriate amount of the standards to prepare a blank spike containing 50 μg/L of each analyte. In situations where lower detection limits are required, a blank spike at 20 μg/L may be prepared. The stock solution for the BS must be from the same source as the initial calibration solution. Refer to Table 8-F for the preparations of the blank spikes.

11.6.2.1 Water and medium-level soil samples - Place a 40 ml vial, filled with DI water onto the autosampler.

11.6.2.2 Low-level soil samples without sodium bisulfate - Aliquot 5 ml of the blank spike into vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.6.2.2.1 Low-level soil samples with sodium bisulfate for Method 5035 - Add 1g of sodium bisulfate to labeled 40 ml vial before aliquot 5 ml of the blank spike into vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.6.3 Initiate auto addition of internal standard and surrogate into the syringe per 11.5.2.

11.6.4 Compare the percent recoveries (% R) (see Section 13.5) to the in-house limits acceptance criteria. If a blank spike is out of control, all the associated samples must be reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote (remark) and no further action is required. Or if the blank spike recovery is low and the hits in the samples are above regulatory levels.

11.6.5 Do not analyze samples and MS/MSD (step 5) unless the BS meets acceptance criteria.

11.6.6 The blank spike and matrix spike must be the same source and concentration.

11.7 Step 5: Samples /MS/MSD analysis

11.7.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

11.7.2 Select the sample dilution factor to assure the highest concentration analyte is above the calibration range midpoint, but below the upper limit of the range depend on project requirements. See Table 9 for dilution guideline.

- Utilize FID screen data.
- Utilize acquired sample data.
- Utilize the history program.
- Sample characteristics (appearance, odor).

11.7.3 Water samples.

11.7.3.1 Using O.I. Model 4560 sample concentrator with 4551 or 4552 vial multisampler,

- Place the 40 ml vial in the tray, or
- Load 5ml sample into purge tube if sample volume limited.

11.7.3.2 A matrix spike and matrix spike duplicate are performed independently by spiking 20ul of the appropriate standards into the 40ml sample vial. If there are not enough vials for this procedure, a matrix spike and a sample duplicate are performed in place of an MS/MSD.

11.7.4 Sediment/ soil sample

11.7.4.1 Low-level soil method

11.7.4.1.1 Collect the sample using the procedures detailed in the SOP for SW846 Method 5035 low - level soil samples.

11.7.4.1.2 Weigh out 5 g of each sample into a labeled, tared vial filled with 5 ml DI water. Add the matrix spike by manually puncturing the septum with a small-gauge needle. Transfer the 40ml vial to the autosampler tray. Stir and heat the sample at the time of analysis.

11.7.4.2 Medium-level soil method

11.7.4.2.1 Collect the sample using the procedures detailed in the SOP for SW846 Method 5035 medium - level soil samples.

11.7.4.2.2 Select a methanol aliquot of appropriate volume (see Table 9) determined via screening and transfer to 40 ml of reagent water.

11.7.5 Program the autosampler to inject the internal standard and surrogate solution into the robotic syringe used to withdraw sample from the 40 ml vial. This addition to 5 ml of sample is equivalent to a concentration of 50 μg/L of each internal standard and surrogate.

11.7.5.1 For O.I. SIM spiker: Automatically adds 5 μl of 50 μg/ml internal standard and surrogate solution (Section 9.4.1.1) to each sample.

11.7.5.2 For O.I. SAM spiker: Automatically adds 1 μl of 250 μg/ml internal standard and surrogate solution (Section 9.4.1.2) to each sample.

11.7.6 Purge the sample for 9 minutes with Helium or Nitrogen.

11.7.6.1 Low-level soil sample must be performed at 40 °C while the sample is being agitated with the magnetic stirring bar or other mechanical means.

11.7.6.2 To improve the purging efficiency of water-soluble compounds, aqueous samples may also be purged at 40 °C as long as all calibration standards (for 1,4-Dioxane SIM option, purge temperature is 80°C), samples and QC samples are purged at the same temperature and acceptable method performance is demonstrated.

11.7.7 One sample is randomly selected from each analytical batch of similar matrix types and spiked in duplicate to determine whether the sample matrix contributes bias to the analytical results. A matrix spike and matrix spike duplicate are performed by spiking the sample for a concentration of 50 μg/l or 50 μg/kg based on 5 g dry weight. In situations where lower detection limits are required, a blank spike at lower concentration may be prepared.

11.7.8 Desorb the sample for a maximum of 4 minutes by rapidly heating the trap to 190 °C while backflushing with Helium. Desorb time may require performance optimization between 0.5 and 4.0 minutes as dictated by trap manufacturers specifications or instrument characteristics.

11.7.9 Program the purge and trap system to automatically rinse purge tube at least twice with heated organic-free water (reagent water) between analyses to avoid carryover of target compounds. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with methanol solution between analyses, rinse it with distilled water.

11.7.10 Bake the trap at least 10 minutes at 210 °C to remove any residual purgeable compounds.

11.7.11 If the initial analysis of the sample or a dilution of the sample has a response for any ion of interest that exceeds the working range of the GC/MS system, the sample must be reanalyzed at a higher dilution.

11.7.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

11.8 Sample dilutions

11.8.1 Using Screening Data to Determine Dilution Factors

11.8.1.1 Dilution for High Concentration Analytes Exceeding the Calibration Range

11.8.1.1.1 The highest concentration target compound detected in the screen data is compared to the highest concentration calibration standard used for determinative volatile organics analysis.

11.8.1.1.1.1 Divide the calibration concentration of the screen concentration by the highest concentration calibration standard.

11.8.1.1.1.2 If the result is >1, sample dilution is considered.

11.8.1.1.2 The result from step 11.8.1.1.1 determines the dilution factor. The dilution factor is targeted to assure that the highest concentration diluted analyte is at the mid-range concentration of the calibration curve for the determinative analysis.

11.8.1.1.3 In all cases a conservative approach to dilution is applied to minimize the increase of detection and reporting limits

11.8.1.2 Dilution for High Concentration Matrix Interferences

11.8.1.2.1 The peak height of the background is compared to the peak height of the later eluting calibration standards from the screening analysis.

11.8.1.2.1.1 A rough estimate of background concentration is calculated by dividing the background peak height by the peak height of the

selected screening standard and multiplying by its concentration.

11.8.1.2.2 If the result is >1, sample dilution is considered.

11.8.1.2.3 The result from step 11.8.1.2.1 determines the dilution factor. The dilution factor is targeted to avoid Carry-over contamination between samples and facilitate qualitative and quantitative analysis of target compounds present in the sample.

11.8.1.2.4 In all cases a conservative approach to dilution is applied to minimize the increase of detection and reporting limits

11.8.2 If the concentration of any target compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and re-analyzed. Until the diluted sample is in a sealed sample vial, all steps in the dilution procedure must be performed without delay.

11.8.3 Water Samples.

11.8.3.1 Prepare all dilutions of water samples in volumetric flasks or Class A graduated cylinder. Intermediate dilutions may be necessary for extremely large dilutions.

11.8.3.2 Calculate the approximate volume of reagent water, which will be added to the volumetric flask or graduated cylinder and add slightly less than this quantity to the flask. Refer to Table 9 for dilution guideline.

11.8.3.3 Inject the proper sample aliquot from a syringe into the volumetric flask or graduated cylinder. It is also permissible to pour the sample directly into a graduated cylinder for some dilutions. Dilute the flask to the volume mark with reagent water. Cap the flask and invert the flask three times.

11.8.3.4 Fill a 40 ml sample vial and seal with a Teflon baked silicon septum, load the diluted sample into the autosampler and analyze according to Section 11.7.

11.8.4 Low-level Soil Samples.

11.8.4.1 Screen data is used to determine the appropriate sample preparation procedure for a sample, the low-level soil method or the medium-level soil method.

11.8.4.2 If any target compound exceeds the initial calibration range from the analysis of 5 g sample, a smaller sample size must be analyzed. However, the smallest sample size permitted is 0.5 g. If smaller than 0.5 g sample size is needed to prevent any target compounds from exceeding the initial calibration range, the medium level method must be used.

11.8.4.2.1 Samples that must use medium level method will be analyzed under separate calibration curve.

11.9 Data interpretation

11.9.1 Qualitative identification.

11.9.1.1 The targeted compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound.

11.9.1.2 The characteristic ions for target compounds that can be determined are listed in Table 7. Table 4 and Table 5 list the characteristic ions for internal standards and surrogate compounds respectively.

11.9.1.3 The criteria required for a positive identification are listed below.

11.9.1.3.1 The sample component must elute at the same retention time (RT) as the daily standard. Criteria are the RT of sample component must be within ± 10 seconds of the standard component (delta RT 0.17 minute) or within ±10 seconds relative to the shift of the associated Internal standard (delta RT of the IS ± 0 seconds).

11.9.1.3.2 The relative intensities of these ions must agree within ± 30 % between the daily standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 20 and 80 %.)

11.9.1.3.2.1 Compounds can have secondary ions outside criteria from co-eluting compounds and/or matrix effect that can contribute to ion abundances. The interference on ion ratios can't always be subtracted out by software programs resulting in qualified compound identification.

11.9.1.3.2.2 Quantitation reports display compounds that have secondary ions outside the ratio criteria with a "#" flag.

11.9.1.3.3 Structural isomers that produce very similar mass spectra must be identified as individual isomers if they have sufficiently different GC retention times. Isomers are considered resolved if the height of the valley between two isomer peaks is less than 50 % of the average of the two peak heights or 1- [valley height]/ [average peak height] is ≥50%. Otherwise, structural isomers are identified as isomeric pairs. The resolution of structural isomers must be verified in the ICV and daily CCV standards to verify if the instrument performance is adequate regarding separation of compound of interest which are structural isomers.

11.9.2 Quantitative analysis

11.9.2.1 Once a target compound has been identified, its concentration (Section 13.4) will be based on the integrated area of the quantitation ion, normally the base peak (Table 7). The compound is quantitated by internal standard technique with an average response factor generated from the initial calibration curve.

11.9.2.2 If the sample produces interference for the primary ion, use a secondary ion to quantitate (see Table 7). This is characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. Also, interference could severely inhibit the response of the internal standard ion. This secondary ion must also be used to generate new calibration response factors.

11.10 Library search for tentatively identified compounds.

11.10.1 If a library search is requested, the analyst must perform a forward library search of NBS or NIST08 mass spectral library to tentatively identify 15 non-reported compounds.

11.10.2 Guidelines for making tentative identification are listed below.

11.10.2.1 These compounds must have a response greater than 10 % of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

11.10.2.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

11.10.2.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.

11.10.2.4 Relative intensities of major ions in the reference spectrum (ions > 10 % of the most abundant ion) must be present in the sample spectrum.

11.10.2.5 The relative intensities of the major ions must agree within ± 20 %. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must between 30 and 70%).

11.10.2.6 Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.

11.10.2.7 Ions present in the reference spectrum but not in the sample spectrum must be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

11.10.2.8 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

11.10.2.9 The resulting concentration must be reported indicating: (1) that the value is estimate, and (2) which internal standard was used to determine concentration. Quantitation is performed on the nearest internal standard.

11.10.2.10 Mass spectral library search algorithm typically assign a match factor to the peak identity based on comparison of an unknown mass spectrum to library

spectra. For spectra meeting the above conditions, match factors greater than 80% may be considered confirming evidence.

11.11 An instrument blank is a system evaluation sample containing lab reagent grade water with internal standards and surrogates. An instrument blank is used to remove and or evaluate residual carryover from high level standards, spike samples and field samples. Since target compound lists have expanded to overlap some volatile and semi-volatile compounds, instrument blanks are necessary to remove carryover contamination.

11.11.1 The compounds that may exhibit carryover for this method are listed in Table 11.

11.11.2 If instrument blanks following a standard or spike sample exhibits carry-over effect, then any samples that show the same carryover profile, after a comparable concentration must be considered suspect and rerun for confirmation. For example, if an instrument blank has 1ppb detected after a 200ppb standard, then any sample following a sample containing 200ppb or above of the same compound must be confirmed for possible carryover.

11.11.3 If an Instrument Blank(s) was run following suspect high concentration samples and it exhibits the same carryover profile after a comparable concentration must be considered suspect and rerun for confirmation.

11.11.4 In some cases, several instrument blanks may have to be run to eliminate contamination from over loaded samples.

11.11.5 The analytical system is considered free of carryover, when no target analytes can be detected above the MDL.

11.12 Selected Ion Monitoring (SIM) Option

11.12.1 Instrument Set-Up: Modify the method for SIM analysis and define ion groups with retention times, ions and dwell times to include base peak ion for the target compounds of interest, surrogates, and internal standards (Table 2a.) Select a mass dwell time of 50 milliseconds for all compounds.

11.12.2 Calibration: Calibrate the mass spectrometer in the selected ion monitoring mode using 9 calibration standards of 0.25, 0.4, 1, 2, 5, 20, 50, 100 and 200 ug/l. Spike each standard with the SIM specific internal standard solution at 5 ug/ml. Calculate individual response factors and response factor RSDs. The initial calibration must meet the criteria in section 10.2.10.

11.12.3 Initial Calibration Verification. Verify the initial calibration after its completion using a 20 ug/l calibration standard purchased or prepared from a second standards reference materials source. The initial calibration verification must meet the criteria from Section 10.3.

11.12.4 Continuing Calibration Verification. Verify the initial calibration every 12 hours using a 5 or 20 ug/l calibration. The continuing calibration verification must meet the criteria from Section 10.4.

11.12.5 Surrogate Standard Calculation. Report surrogate spike accuracy for the surrogates spiked for the full scan GC/MS analysis.

12.0 QUALITY CONTROL

12.1 QC Requirements Summary

BFB	Beginning of the analytical shift
ICV - Second Source Calibration Check Standard	Following initial calibration
Calibration Verification Standard	Every 12 hours
Method Blank	Every 12 hours
Blank Spike	One per analytical batch*
Matrix Spike	One per analytical batch*
Matrix Spike Duplicate or Sample DUP (depends on sample volume)	One per analytical batch*
Surrogate	Every sample and standard
Internal Standard	Every sample and standard

*The maximum number of samples per analytical batch is twenty.

12.2 Daily GC/MS Performance Check - BFB

12.2.1 Refer to Section 11.3.

12.3 Second Source Calibration Check Standard

12.3.1 Refer to Section 10.3.

12.3.2 Calibration Verification Standard

12.3.3 Refer to Section 10.4.

12.4 Method Blank

12.4.1 Refer to Section 11.5

12.5 Blank Spike

12.5.1 Refer to Section 11.6

12.6 Matrix Spike (MS)/Matrix Spike Duplicate (MSD)

12.6.1 One sample is selected at random from each analytical batch of similar matrix types and spiked in duplicate to check precision and accuracy.

12.6.2 Assess the matrix spike recoveries (Section 13.5) and relative percent difference (RPD) (Section 13.6) against the control limits.

12.6.3 If the matrix spike recoveries do not meet the criteria, check the blank spike recovery to verify that the method is in control. If the blank spike did not meet criteria, the method is

out of control for the parameter in question and must be reanalyzed or qualified with an estimate of potential bias. Otherwise, matrix interference is assumed and the data is reportable. No further corrective action is required.

12.7 Surrogates

12.7.1 All standards, blanks, samples, and matrix spikes contain surrogate compounds, which are used to monitor method performance. If the recovery of any surrogate compound does not meet the control limits, the result must be flagged and:

12.7.1.1 The calculation must be checked.

12.7.1.2 The sample must be reanalyzed if the recovery of any one surrogate is out of control limit.

12.7.2 If the sample exhibits matrix interference, defined as excessive signal levels from target or non-target interfering peaks. In this case, reanalysis may not be required following team leader/manager approval.

12.7.3 If surrogate recoveries are acceptable upon reanalysis, the data from the reanalysis is reported. If the reanalysis date did not meet the hold time, then both sets of data must be submitted with the reanalysis reported.

12.7.4 If surrogates are still outside control limits upon reanalysis, then both sets of data must be submitted with the first analysis reported.

12.8 Internal Standard

12.8.1 Retention time for all internal standards must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 50 µg/l standard of initial calibration

12.8.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area in the latest calibration standard (12 hr. time period).

12.8.3 If area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

12.8.4 If areas are acceptable upon reanalysis, the reanalysis data is reported.

12.8.5 If areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

13.0 CALCULATION

13.1 Response Factor (RF)

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

where:
As = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cs = Concentration of the compound being measured (ug/l).
Cis = Concentration of the specific internal standard (ug/l).

13.2 Percent Relative Standard Deviation (% RSD)

$$\%RSD = \frac{SD}{RFav} \times 100$$

where:
SD = Standard Deviation
RFav = Average response factor from initial calibration.

13.3 Percent Difference (%D)

$$\%D = \frac{(RFav - RFcv)}{RFav} \times 100$$

where:
RFcv = Response factor from Calibration Verification standard.
RFav = Average response factor from initial calibration.

13.4 Concentration (Conc.)

For water:

$$\text{Conc. } (\mu g/l) = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Vi}$$

For soil/sediment low level (on a dry weight basis):

$$\text{Conc. } (\mu g/kg) = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Ws \times M}$$

For soil/ sediment medium level (on a dry weight basis)

$$\text{Conc. } (\mu g/kg) = \frac{Ac \times Cis \times Vp \times Vt}{Ais \times RF \times Vme \times Ws \times M}$$

Where:
Ac = Area of characteristic ion for compound being measured.
Ais = Area of characteristic ion for internal standard.
Cis = Concentration of internal standard
RF = Response factor of compound being measured(from initial calibration)
Vi = Initial volume of water purged (ml)
Vp = 5 ml (Total Purge Volume)
Vme = Volume of Methanol aliquot

Vt = Ml Solvent + ((100-% solid)/100 x Ws)
Ws = Weight of sample extracted (g).
M = (100 - % moisture in sample) / 100 or % solids / 100

13.5 Percent Recovery (% R)

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

13.6 Relative Percent Difference (RPD)

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

Where:
MSC = Matrix Spike Concentration
MSDC = Matrix Spike Duplicate Concentration

13.7 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{a} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

13.8 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient

x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

13.9 Quadratic curve with internal standard technique

$$Cs = \frac{-b \pm \sqrt{b^2 - 4a\left(c - \frac{A_s \times C_{is}}{A_{is}}\right)}}{2a}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

14.0 DOCUMENTATION

14.1 The Analytical Logbook. The logbook must be completed by the analyst daily. Each instrument will have a separate logbook. The daily sequence must be recorded in the logbook by giving a file number to every instrument standard, QC, and samples in appropriate spaces. The files must be never overwritten or skipped intentionally. In case where the file is skipped or overwritten, a thorough explanation must be documented in the notes section. Upon completion, every analytical batch must be reviewed and signed by a supervisor/team lead. Supervisor signature indicates all documentation was performed correctly.

14.1.1 If samples or blank spike require reanalysis, a brief explanation of the reason and corrective action must be documented in the Comments section.
14.1.2 If maintenance was done on the instrument in order to pass the CCV or any other reason, the analyst must document it in the logbook.

14.2 Standards Preparation Logbook must be completed for all standard preparations. All information must be completed; the page must be signed and dated by the appropriate person.

14.2.1 The SGS lot number must be cross-referenced on the standard vial.

14.3 Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory personnel must review and sign all laboratory logbooks monthly to ensure that information was recorded properly. Additionally, the instrument maintenance logbooks and the accuracy of the recorded information must also be verified and signed off on the first page of the logbook quarterly by a supervisor/team lead.

14.6 Acrolein and Acrylonitrile data reported from a preserved sample must be footnoted: “Results reported from the HCl preserved sample. This reported result can only be used for screening purposes for Acrolein and Acrylonitrile.” Any samples analyzed form an unpreserved vial must be footnoted stating samples were unpreserved and analyzed within 7 days.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non-hazardous aqueous wastes

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

Table 1 TARGET COMPOUNDS		
Acetone	1,4-Dichlorobenzene	Methylene Bromide
Acetonitrile	Dichlorodifluoromethane	Methylene Chloride
Acrolein	1,1-Dichloroethane	1-Methylnaphthalene
Acrylonitrile	1,2-Dichloroethane	2-Methylnaphthalene
Allyl Chloride	1,1-Dichloroethene	Naphthalene
Benzene	cis-1,2-Dichloroethene	2-Nitropropane
Benzyl chloride	trans-1,2-Dichloroethene	Pentachloroethane
Bromobenzene	1,2-Dichloropropane	Propionitrile
Bromochloromethane	1,3-Dichloropropane	Propyl Acetate
Bromodichloromethane	2,2-Dichloropropane	n-Propylbenzene
Bromoform	1,1-Dichloropropene	Styrene
Bromomethane	cis-1,3-Dichloropropene	Tert Butyl Alcohol
2-Butanone (MEK)	trans-1,3-Dichloropropene	tert-Amyl Methyl Ether
Butyl Acetate	1,4-Dioxane	tert-Butyl Ethyl Ether
n-Butyl Alcohol	Epichlorohydrin	1,1,1,2-Tetrachloroethane
n-Butylbenzene	Ethyl Acetate	1,1,2,2-Tetrachloroethane
sec-Butylbenzene	Ethyl Ether	Tetrachloroethene
tert-Butylbenzene	Ethyl Methacrylate	Tetrahydrofuran
Carbon Disulfide	Ethylbenzene	Toluene
Carbon Tetrachloride	p-Ethyltoluene	trans-1,4-Dichloro-2-Butene
Chlorobenzene	Freon 113	1,2,3-Trichlorobenzene
Chlorodifluoromethane	Heptane	1,2,4-Trichlorobenzene
Chloroethane	Hexachlorobutadine	1,1,1-Trichloroethane
2-Chloroethyl Vinyl Ether	Hexachloroethane	1,1,2-Trichloroethane
Chloroform	Hexane	Trichloroethene
Chloromethane	2-Hexanone	Trichlorofluoromethane
Chloroprene (2-chloro-1,3-butadiene)	Iodomethane (Methy iodide)	1,2,3-Trichloropropane
o-Chlorotoluene	IsoAmyl Alcohol	1,2,4-Trimethylbenzene
p-Chlorotoluene	Isobutyl Alcohol	1,3,5-Trimethylbenzene
Cyclohexane	Isopropyl Acetate	2,2,4 Trimethylpentane
Cyclohexanone	Isopropylbenzene	Vinyl Acetate
di-Isobutylene	p-Isopropyltoluene	Vinyl Chloride
di-Isopropyl Ether	Methacrylonitrile	Vinyltoluene
1,2-Dibromo-3-Chloropropane	Methyl Acetate	m,p-Xylene
Dibromochloromethane	3 Methyl-1-Butanol	o-Xylene
1,2-Dibromoethane	Methyl Tert Butyl Ether	Ethanol
Dibromomethane	Methylcyclohexane	Methyl Acrylate
1,2-Dichlorobenzene	Methyl Methacrylate	1-chloro-1,1-difluoroethane
1,3-Dichlorobenzene	4-Methyl-2-pentanone (MIBK)	1,1,1-trifluoroethane
1,1-dichloro-1-fluroethane	2,2-Dichloropropane	1,3-Butadiene
3,3-Dimethyl-1-Butanol	Tert-Butyl Formate	Tert-amyl alcohol
2-methylnaphthalene	1,2,3-Trimethylbenzene	

Table 2 RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/ Mass Spectrometer	
Carrier Gas (linear velocity)	Helium at *30 cm/sec (or hydrogen)
Mass range	35 – 270 amu *
Electron Energy	70 volts (nominal)
Scan time	not to exceed 2 sec. per scan
Injection port temperature	200 - 225 °C
Source temperature	200 - 250 °C
Transfer line temperature	220 - 280 °C
Analyzer temperature	220 - 250 °C
Gas Chromatograph temperature program*	
Initial temperature	*40 °C
Time 1	*3 minutes
Column temperature rate	*8 degrees/min.
Final temperature	*220 °C.- 240 °C
Total run time	*25 – 50 mins
Split ratio	*20:1
Purge and Trap Device	
Purge time	9 min. (at 40 °C for low-level soil) SIM – 6 min @ 80 °C
Purge gas	Helium or Nitrogen
Desorb**	1 min. at 190 °C
Bake	>10 min. at 210 °C
Transfer line	100 - 130 °C
Valve temperature	approx. transfer line temperature

(*) Parameter modification allowed for performance optimization provided operational and QC criteria is achieved. (must be approved by team leader/manager)

(**) Desorb time may require performance optimum between 0.5 and 4.0 minutes as dictated by trap manufacturers specifications or instrument characteristics

Table 2a SIM Group Parameters		
Group No.	**Retention Time (minutes)**	**Ions**
1	0 – 10.8	58, 65, 66, 88
2	10.8 – 16.0	95, 174, 176, 96,64

Table 3 BFB KEY IONS AND ION ABUNDANCE CRITERIA	
Mass	**Ion Abundance Criteria**
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5-9% of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Table 4 INTERNAL STANDARD QUANTITION IONS	
Internal Standard	**Primary/Secondary Ions**
1,4-Difluorobenzene	114 / 63,88
Chlorobenzene-d5	117 / 82, 119
Pentafluorobenzene	168
1,4-Dichlorobenzene-d4	152 / 115, 150
Tert Butyl Alcohol-d9	65/66
Internal Standard (SIM)	
4-BFB	95/174,176

Table 5 SURROGATE QUANTITION IONS	
Surrogate Compound	**Primary/Secondary Ions**
1,2 Dichloroethane – d_4	102
Dibromofluoromethane	113
Toluene-d8	98
4-Bromofluorobenzene	95 / 174, 176
1,4-dioxane-d8	96, 64

Table 7 Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)	Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Tert Butyl Alcohol-d9	65		Dibromomethane	93	95, 174
Tert Butyl alcohol	59	57	Di-isobutylene	57	
Ethanol	45	46	Epichlorohydrin (pp)	57	57, 49, 62, 51
1,4-Dioxane (pp)	88	58,43,57	Heptane	57	
Pentafluorobenzene	168		Methyl cyclohexane	83	
1,1,1-Trichloroethane	97	99, 61	Methyl methacrylate	100	69, 41, 39
1,1-Dichlorethane	63	65, 83	n-Butanol (pp)	56	41
1,1-Dichloroethene	96	61, 63	Propyl Acetate	43	
2,2-Dichloropropane	77	97	tert Amyl Methyl Ether	73	
2-Butanone (pp)	72	43, 72	Trichloroethene	95	97, 130, 132
Acetone (pp)	58	43	**Chlorobenzene-d5**	117	82,119
Acetonitrile (pp)	41	41, 40, 39	1,1,1,2-Tetrachloroethane	131	133, 119
Acrolein (pp)	56	55,58	1,3-Dichloropropane	76	78
Acrylonitrile (pp)	53	52, 51	Bromoform	173	175, 254
Allyl Chloride	76	41	Butyl Acetate	56	
Bromochloromethane	128	49, 130	Chlorobenzene	112	77, 114
Bromomethane	94	96	Dibromochloromethane	129	127
Carbon disulfide	76	78	Ethylbenzene	91	106
Carbon tetrachloride	117	119	m-Xylene	106	91
Chlorodifluouromethane	51	86	o-Xylene	91	106
Chloroethane	64	66	3,3-Dimethyl-1-Butanol	57	69
Chloroform	83	85	p-Xylene	106	91
Chloromethane	50	52	Styrene	104	78
Chloroprene	53	53, 88, 90, 51	Ethyl methacrylate	69	69, 41, 99, 86, 114
cis-1,2-Dichloroethene	96	61, 98	Toluene	92	91
Cyclohexane	84		**Toluene-d_8 (S)**	98	
Dibromofluoromethane (S)	113		Tetrachloroethene	164	129,131,166
Dichlorodifluoromethane	85	87	Cyclohexanone	55	
1,1-Dichloropropene	75	110, 77	2-Hexanone (pp)	58	43, 57, 100
Diethyl ether	74	45, 59	trans-1,3-Dichloropropene	75	77, 39
1,3-Butadiene	54		**1,4 Dichlorobenzene-d4**	152	115,150
Diisopropyl ether	45	102	1,1,2,2-Tetrachloroethane	83	131, 85
Ethyl acetate (pp)	45	43, 88, 61	1,2,3-Trichlorobenzene	180	182, 145
Ethyl tert Butyl Ether	59		1,2,3-Trichloropropane	110	77,75
Hexane	56		1,2,4-Trichlorobenzene	180	182, 145
Isopropyl acetate	87	43	1,2,4-Trimethylbenzene	105	120

Table 7 Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)	Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Tert-Amyl alcohol	59	73,55	1,2-Dibromo-3-chloropropane(pp)	157	155, 75
Freon 113	151		1,2-Dichlorobenzene	146	111,148
Iodomethane	142	127, 141	1,3,5-Trimethylbenzene	105	120
Isobutyl alcohol (pp)	43	43, 41, 42, 74	1,3-Dichlorobenzene	146	111, 148
Methacrylonitrile (pp)	67	41, 39, 52, 66	1,4-Dichlorobenzene	146	111, 148
Methyl Acetate	43	74	2-Chlorotoluene	126	91
Methylene chloride	84	86, 49	**4-Bromofluorobenzene (S)**	95	174, 176
Methyl-t-butyl ether	73	57	2-methylnaphthalene	142	141,115,143
Propionitrile (ethyl cyanide)(pp)	54	54, 52, 55, 40	Dibromofluoromethane		
Tetrahydrofuran	71	42	4-Chlorotoluene	91	126
trans-1,2-Dichloroethene	96	61, 98	Benzyl chloride	91	91, 126, 65, 128
Trichlorofluoromethane	101	151, 153	Bromobenzene	156	77, 158
Vinyl acetate	86	43	Hexachlorobutadiene	225	223, 227
Vinyl chloride	62	64	Hexachloroethane (pp)	201	166, 199, 203
Methyl Acrylate	85	55	Isopropylbenzene	105	120
Tert-Butyl Formate	59	57, 41	Naphthalene	128	-
1-chloro-1, 1-difluoroethane	65	45,85	n-Butylbenzene	92	91, 134
1,1,1-trifluoroethane	69	69,45	n-Propylbenzene	91	120
1,1-dichloro-1-fluroethane	81	45,61	Pentachloroethane (pp)	167	167,130,132,165,169
2,2-Dichloropropane	77	97,79	p-isopropyltoluene	119	134,91
1,2,3-Trimethyl benzene	105	120,119			
1,4 Difluorobenzene	114	63, 88	sec-Butylbenzene	105	134
1,1,2-Trichloroethane	83	97, 85	tert-Buytlbenzene	119	91, 134
1,2-Dibromoethane	107	109, 188	trans-1,4-Dichloro-2-butene (pp)	53	88, 75
1,2 Dichloroethane	62	98			
1,2 Dichloropropane	63	112	**(pp) = Poor Purging Efficiency**		
2,2,4 Trimethylpentane	57		(S)=Surrogate		
2-Chloroethyl-vinylether (pp)	63	65, 106			
Dichloroethane-d_4 (S)	65	102			
2-Nitropropane	46	-			
3 Methyl –1 butanol	70	55			
4-Methyl-2-pentanone (pp)	58	43, 85, 100			
Benzene	78	-			
Bromodichloromethane	83	85, 127			
cis-1,3-Dichloropropene	75	77, 39			
Methylcyclohexane	83				

Table 7-1 SIM - Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
4-BFB	95	174, 176
1,4-Dioxane	88	58
1,4-dioxane-d8	96	64

Table 8 STANDARDS PREPARATION

A) Internal standard and Surrogate mixtures:

	a) 50/500 μg/ml	b) 250/2,500 μg/ml
Internal Standard Mixture (20,000 μg/ml)	0.25 ml	3.125 ml
Tert Butyl Alcohol-d_9 (50,000 μg/ml)	1.0 ml	12.5 ml
Surrogate Mixture (10,000 μg/ml)	0.5 ml	6.25 ml
Methanol	98.25 ml	228.125 ml
Total	100 ml	250 ml

- 50/500 μg/ml internal standard and surrogate mixture: The mixture is prepared by measuring 0.25 ml of 20,000 μg/ml Internal Standard Mixture (Ultra or equivalent), 1.0 ml of 50,000 μg/ml TBA-d_9 (Absolute or equivalent), 0.5 ml of 10,000 μg /ml Method 8260A Surrogate Standard Mixture (Absolute or equivalent) and bringing to 100 ml with methanol.

- 250/2,500 μg/ml internal standard and surrogate mixture: The mixture is prepared by measuring 3.125 ml of 20,000 μg/ml Internal Standard Mixture (Ultra or equivalent), 12.5 ml of 50,000 μg/ml TBA-d_9 (Absolute or equivalent), 6.25 ml of 10,000 μg /ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 250 ml with methanol.

B) Bromofluorobenzene (BFB):

	a) 25 μg/ml	b)) 250 μg/ml
BFB (25,000 μg/ml)	0.1 ml	0.1 ml
Methanol	99.9 ml	9.9 ml
Total	100 ml	10 ml

- 25 μg/ml solution for direct injection: The BFB is prepared at 25 μg /ml by measuring 0.1 ml of 25,000 μg /ml (Absolute Stock or equivalent) and diluting to 100 ml with methanol.

- 250 μg /ml solution for purging: The BFB is prepared at 250 μg /ml by measuring 0.1 ml of 25,000 μg /ml (Absolute Stock or equivalent) and diluting to 10 ml with methanol.

C) Secondary dilution standards:

2nd Dilution Standards	Stock Solution	Concentration (μg/ml)	Volume Added (μl)	Final Volume in Methanol (ml)	Final Concentration (μg/ml)
V8260 Mixture	502.2 CAL2000 Mega Mix	2,000	5,000	100	100
	524 Cal Mix 7A	2,000	5,000		100
	524 Cal Mix 8	2,000	5,000		100
	Ketone mix	20,000	1,500		300
	Multiple neat compounds	Neat			100
	Multiple single component standards	5000-20,000	500-2000		100
Acrolein	Acrolein	Neat (95%)	12.5	100 (4:1 ratio of DI water : methanol)	100

Gas Mixture	VOC Gas Mixture	2,000	1,250	25	100
	Cyclohexane	neat	3.2		100

- 100 μg /ml V8260 mixture: The mixture is prepared at 100 μg /ml by measuring 5 ml of 2,000 μg/ml 502.2 Mega Mix stock standard, 5 mL of 2,000 μg/ml 524 Cal Mix 7A, 5 mL of 2,000 μg/ml 524 Cal Mix 8, appropriate amount of some neat compounds and single component standards, and bringing to 100 ml with methanol.

- 100 μg/ml V8260 Acrolein: The mixture is prepared at 100 μg/ml by measuring 12.5 μl of 95% acrolein to 100 ml of a 4:1 ratio of DI water:methanol to reduce the amount of methanol injected into the system per run.

- 100 μg /ml gas mixture ***: The mixture is prepared at 100 μg /ml by measuring 1.25 ml of 2,000 μg/ml stock standard, 3.2 μl of neat cyclohexane and bring to 25 ml with methanol.
  ******* Gas mixture must be prepared weekly.

D).1 Initial Calibration Standards: using DI water bring to 50 ml final volume for the 1 -400 ppb standards and 500 ml for the 0.2 and 0.5 ppb standards: All mixtures used must be **secondary dilution** standards at **100 ppm**. Note: Larger volumes may be prepared if needed i.e. if 100 ml final volume is used the volume of the standard added would be doubled.

Standard and Surrogate Concentration	V8260 Mix (100 ppm)	V8260 Acrolein (100 ppm)	Gas compound Mix (100 ppm)	Surrogate Mix when added manually (100ppm)
0.2 ppb	1.0 μl	1.0 μl	1.0 μl	1.0 μl#
0. 5 ppb	2.5 μl	2.5 μl	2.5 μl	2.5 μl#
1 ppb	0.5 μl	0.5 μl	0.5 μl	0.5 μl#
2 ppb *	1.0 μl	1.0 μl	1.0 μl	1.0 μl#
4 ppb *	2.0 μl	2.0 μl	2.0 μl	2.0 μl#
5 ppb	2.5 μl	2.5 μl	2.5 μl	2.5 μl#
8 ppb *	4.0 μl	4.0 μl	4.0 μl	4.0 μl#
10 ppb *	5 μl	5 μl	5 μl	5 μl#
20 ppb	10 μl	10 μl	10 μl	10 μl#
50 ppb	25 μl	25 μl	25 μl	25 μl#
100 ppb	50 μl	50 μl	50 μl	50 μl#
200 ppb	100 μl	100 μl	100 μl	100 μl#
300 ppb *	150 μl	150 μl	150 μl	150 μl#
400 ppb *	200 μl	200 μl	200 μl	200 μl#

* depending upon the instrument.
\# See Section 10.2.2.1 for correction factor.

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of each standard into vial if applicable. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

Table 8 STANDARD PREPARATION (Continued)

D).2 Initial Calibration Standards for 1,4-Dioxane using SIM

Standard Concentration (ppb)	1,4-Dioxane Solution (100ppm)	DI Water – Final Volume (ml)
0.25	1.25 µl	500
0.4	2 µl	500
1	1 µl	100
2	2 µl	100
5	2.5 µl	50
20	10 µl	50
50	25 µl	50
100	50 µl	50

E) C**ontinuing Calibration Standard: using DI water bring to 50 ml final volume:** All mixtures used are secondary dilution standards at 100 ppm.

Concentration	V8260 Mix (100 ppm)	V8260 Acrolein (100 ppm)	Gas compound Mix (100 ppm)
50 ppb	25 µl	25 µl	25 µl

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the continuing calibration standard into vial if applicable. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

F) Blank Spike (BS): using DI water bring to 50 ml final volume: All mixtures used are 100 ppm secondary dilution standards.

Concentration	V8260 Mix (100 ppm)	V8260 Acrolein (100 ppm)	Gas compound Mix (100 ppm)
50 ppb	25 ul	25 ul	25 ul

For lower detection level required (test code: V8260LL)

Concentration	V8260 Mix (100 ppm)	V8260 Acrolein (100 ppm)	Gas compound Mix (100 ppm)
20 ppb	10 ul	10 ul	10 ul

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the blank spike into vial if applicable. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

Table 9 GUIDELINE FOR DILUTION PREPARATION
Water Sample

Dilution	Sample amount taken	Final volume A (volumetric)	Take from final volume A	Final volume B (volumetric)
1:2	25 ml	50 ml		
1:5	10 ml	50 ml		
1:10	5 ml	50 ml		
1:20	2.5 ml	50 ml		
1: 25	2 ml	50 ml		
1:50	1 ml	50 ml		
1:100	0.5 ml	50 ml		
1:200	250 µl	50 ml		
1:250	200 µl	50 ml		
1:500	100 µl	50 ml		
1:1000	50 µl	50 ml		
1:2000	25 µl	50 ml		
1:2500	20 µl	50 ml		
1:5000	10 µl	50 ml		
1:10000	0.5 ml	50 ml	0.5 ml	50 ml
1:20000	0.5 ml	50 ml	250 µl	50 ml
1:25000	0.5 ml	50 ml	200 µl	50 ml
1:50000	0.5 ml	50 ml	100 µl	50 ml
1:100000	0.5 ml	50 ml	50 µl	50 ml

Soil-Low level (Non-Encore sample)

Dilution	Sample amount taken	Final volume
1:2	2.5 gram	5 ml
1:5	1 gram	5 ml
1:10	0.5 gram	5 ml

Soil-medium level

Additional Dilution	Sample in Methanol amount taken	Final volume (volumetric)
1:1	1 ml	50 ml
1:2	0.5 ml	50 ml
1:5	200 µl	50 ml
1:10	100 µl	50 ml
1:20	50 µl	50 ml
1: 25	40 µl	50 ml
1:50	20 µl	50 ml
1:100	10 µl	50 ml
1:200	5 µl	50 ml
1:250	4 µl	50 ml
1:500	2 µl	50 ml

Table 10 REPORTING LIMITS

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Chlorodifluoromethane	5	5	Chloroform	1	2
Dichlorodifluoromethane	2	5	Freon 113	5	5
Chloromethane	1	5	Methacrylonitrile	10	10
Vinyl chloride	1	2	Butyl Acetate	5	5
Bromomethane	2	5	1,1,1-Trichloroethane	1	2
Chloroethane	1	5	Heptane	5	5
Trichlorofluoromethane	2	5	n-Propyl acetate	5	5
Ethyl ether	2	2	2-Nitropropane	10	10
Acrolein	10	10	Tetrahydrofuran	10	10
1,1-Dichloroethene	1	1	2-Chloroethyl Vinyl Ether	10	25
Tertiary butyl alcohol	10	25	n-Butyl alcohol	250	250
Acetone	10	10	Cyclohexane	5	2
Methyl acetate	5	5	Carbon Tetrachloride	1	2
Allyl chloride	5	5	1,1-Dichloropropene	1	2
Acetonitrile	100	100	Isopropyl Acetate	5	5
Iodomethane	2	5	Benzene	0.5	0.5
Isobutyl alcohol	50	50	1,2-Dichloroethane	1	1
Carbon disulfide	2	2	Trichloroethene	1	1
Methylene chloride	2	5	Methyl methacrylate	10	10
Methyl tert butyl ether	1	1	1,2-Dichloropropane	1	1
Trans-1,2-Dichloroethene	1	1	2-ethylhexyl acrylate	2	2
Di-isopropyl ether	2	2	Dibromomethane	1	5
2-Butanone	10	10	1,4-Dioxane	130	130
1,1-Dichloroethane	1	1	Bromodichloromethane	1	2
Hexane	5	5	cis-1,3-Dichloropropene	1	2
Chloroprene	5	5	4-Methyl-2-pentanone	5	5
Acrylonitrile	10	10	Toluene	1	1
Vinyl acetate	10	10	trans-1,3-Dichloropropene	1	2
Ethyl acetate	5	5	Ethyl methacrylate	10	10
2,2-Dichloropropane	1	2	1,1,2-Trichloroethane	1	2
Cis-1,2-Dichloroethene	1	1	2-Hexanone	5	5
Bromochloromethane	1	5	Cyclohexanone	50	200

Table 10 REPORTING LIMITS (Continued)

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Tetrachloroethene	1	2	4-Chlorotoluene	2	2
1,3-Dichloropropane	1	2	1,3,5-Trimethylbenzene	2	2
Dibromochloromethane	1	2	tert-Butylbenzene	2	2
1,2-Dibromoethane	1	1	1,2,4-Trimethylbenzene	2	2
Chlorobenzene	1	2	sec-Butylbenzene	2	2
1,1,1,2-Tetrachloroethane	1	2	1,3-Dichlorobenzene	1	1
Ethylbenzene	1	1	p-Isopropyltoluene	2	2
m,p-Xylene	1	1	1,4-Dichlorobenzene	1	1
o-Xylene	1	1	1,2-Dichlorobenzene	1	1
Styrene	1	2	n-Butylbenzene	2	2
Bromoform	1	5	1,2-Dibromo-3-choropropane	2	2
Isopropylbenzene	1	2	1,2,4-Trichlorobenzene	1	5
Bromobenzene	1	5	Hexachlorobutadiene	2	5
1,1,2,2-Tetrachloroethane	1	2	Naphthalene	5	5
Trans-1,4-Dichloro-2-butene	5	5	1,2,3-Trichlorobenzene	1	5
1,2,3-Trichloropropane	2	5	Epichlorohydrin	100	100
n-Propylbenzene	2	2	3-Methyl-1-butanol	50	100
2-Chlorotoluene	2	2	Hexachloroethane	2	5
Ethanol	100	200	Methyl Acrylate	5	5
Benzyl Chloride	5	5	Methylcyclohexane	5	2
2,2,4-Trimethylpentane	5	5	1,1,1-trifluoroethane (Freon 143a)	5	5
1-chloro-1,1-difluoroethane (Freon 142b)	5	5	1,1-dichloro-1-fluoroethane (Freon 141b)	5	5
1,3-Butadiene	5	5	Pentachloroethane	5	5
1.4-Dioxane (SIM)	0.4	5	2-methylnaphthalene	5	5
Tert-Butyl Formate	5	5	Tert-amyl alcohol	25	25
1,2,3-Trimethylbenzene	2	2			

Table 11 COMPOUNDS THAT MAY EXHIBIT CARRYOVER

Compound
1,2,4-Trichlorobenzene
Hexachlorobutadiene
Naphthalene
1,2,3-Trichlorobenzene

Table 12 GUIDANCE MINIMUM RELATIVE RESPONSE FACTOR CRITERIA

Compound	Minimum Response Factor	Typical Response Factor
Dichlorofluoromethane	0.100	0.327
Chloromethane	0.100	0.537
Vinyl chloride	0.100	0.451
Bromomethane	0.100	0.255
Chloroethane	0.100	0.254
Trichlorofuoromethane	0.100	0.426
1,1-Dichloroethene	0.100	0.313
Freon 113	0.100	0.302
Acetone	0.100	0.151
Carbon Disulfide	0.100	1.163
Methyl Acetate	0.100	0.302
Methylene chloride	0.100	0.380
trans-1,2 Dichloroethene	0.100	0.351
cis-1,2 Dichloroethene	0.100	0.376
Methyl tert-butyl Ether	0.100	0.847
1,1 Dichloroethane	0.200	0.655
2-Butanone	0.100	0.216
Chloroform	0.200	0.557
1,1,1 Trichloroethane	0.100	0.442
Cyclohexane	0.100	0.579
Carbon Tetrachloride	0.100	0.353
Benzene	.0.500	1.368
1,2 Dichloroethane	0.100	0.443
Trichloroethene	0.200	0.338
Methylcyclohexane	0.100	0.501
1,2-Dichloropropane	0.100	0.382
Bromodichloromethane	0.200	0.424
cis-1,3-Dichloropropene	0.200	0.537
trans-1,3-dichloropropene	0.100	0.515

Table 12 cont'd Compound	Minimum Response Factor	Typical Response
Tetrachloroethene	0.200	0.606
2-Hexanone	0.100	0.536
Dibromochloromethane	0.100	0.652
1,2-Dibromoethane	0.100	0.634
Chlorobenzene	0.500	1.733
Ethyl benzene	0.100	2.827
m,p-Xylene	0.100	1.080
o-Xylene	0.300	1.073
Styrene	0.300	1.916
Bromoform	0.100	0.413
Isopropylbenzene	0.100	2.271
1,1,2,2-Tetrachloroethane	0.300	0.782
1,3-Dichlorobenzene	0.600	1.408
1,4-Dichlorobenzene	0.500	1.427
1,2-Dichlorobenzene	0.400	1.332
1,2-Dibromo-3-chloropropane	0.050	0.129
1,2,4-Trichlorobenzene	0.200	0.806
1,3-Butadiene	0.100	0.250
3,3-Dimethyl-1-butanol	0.010	0.020
1,4-Dioxane (SIM)	0.010	0.286
4-Methyl-2-Pentanone	0.100	0.363
Toluene	0.400	1.577
1,1,2-Trichloroethane	0.100	0.518

Current Version Revision Information

Changes / Edits made (this should include added or deleted information within a sentence or paragraph only):

Section / Subsection	Detailed description of what was revised
Table 1	Added 1,2,3-Trimethylbenzene
Table 7	Added 1,2,3-Trimethylbenzene
Table 10	Added 1,2,3-Trimethylbenzene

Sections or Subsections deleted:

Section / Subsection	Reason section or subsection was removed

Sections or Subsections added:

Section / Subsection	Reason section or subsection was added

History of Revisions

Version #	Date of Revision	Revised By
01	01/20/2021	Maria Ruschke

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